

## Processing and Photostability of Pyrromethene 567 Polycerams

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**Abstract.** Polyceram materials are attractive hosts for laser dyes because they can have high optical transparencies, high laser damage thresholds, and the ability to tailor optical properties by varying the composition and synthetic routes. Pyrromethene 567 has been successfully incorporated within silica : polydimethylsiloxane (PDMS) Polycerams to obtain polishable, crack-free, transparent monoliths using the sol-gel process. Fluorescence photostability was measured by pumping with a  $Q$ -switched, frequency doubled Nd : YAG laser (532 nm) at a pulse rate of 10 Hz. Fluorescence intensity dropped to 50% after approximately 50,000 pulses at a fluence of 0.10 J/cm<sup>2</sup>. UV degradation studies were performed on Polycerams with different polymer contents, and the absorption photostability is related to the solubility and type of caging of the dye.

**Keywords:** laser dyes, pyrromethene-BF<sub>2</sub> complexes, photostability, Polyceram, solid-state laser

### 1. Introduction

A new class of dye complexes, pyrromethene-BF<sub>2</sub>, have received much attention as highly efficient, highly photostable laser dyes. These dyes fluoresce in the same region of the spectrum as rhodamine dyes (550-650 nm), and are planar leading to high quantum yields ( $\phi_f = .995$ ). Low triplet state populations (one-fifth of that of other laser dyes) and low triplet-triplet absorption greatly enhance the photostability. In addition, the BF<sub>2</sub> aids in reducing the number of resonances of the pyrromethene, preventing dye destruction pathways in the excited state. When pumped with 2 W of 532 nm laser light, Pyrromethene 567 showed twice the efficiency of Rhodamine 6G when dissolved in propylene glycol monophenyl ether [1]. A number of chemical substitutions of pyrromethene dyes have been examined and substitutions on the 2,6 positions with auxochromic groups has resulted in the lowest triplet state populations [2].

There is much research effort in producing a solid-state dye laser which would eliminate numerous

problems associated with liquid dye lasers such as dye/solvent pumping and poisoning. The mechanism of photodegradation occurs by the interaction of the dye molecules in the excited state with other species (e.g., impurities, other dye molecules, singlet state oxygen). These photochemical pathways can be suppressed by caging or trapping the dyes within a solid host. In the past several years, pyrromethene-BF<sub>2</sub> complexes have been doped in polymer and sol-gel hosts [3-7]. Lasing action with high slope efficiencies (85%) has been achieved, but there is still a need to improve photostability to increase laser lifetime.

To improve photostability, an inherently photostable dye as well as high optical quality host must be chosen. In addition, controlling the molecular environment of the dye (e.g., homogeneous dye distribution, dye caging, removal of impurities) can play a role in decreasing degradation. Previous investigations of silica : PDMS Polycerams as films for optical waveguides have shown superior optical transparency with low optical losses of <0.15 dB/cm and the materials are attractive hosts for laser dyes [8]. The objective of the

present work was to synthesize transparent, crack-free monoliths of PM-567 Polycerams and to examine their photostability as function of host composition.

## 2. Experimental

2,6-diethyl-1,3,5,7,8-pentamethylpyrromethene-difluoroborate complex (Pyrromethene 567 or PM-567) was synthesized via the route described by Shah et al. [9]. Kryptopyrrole was reacted with acetyl chloride in dichloromethane to yield a 2,6-diethyl-1,3,5,7,8-pentamethylpyrromethene hydrochloride salt. The salt was then reacted with boron trifluoride etherate in the presence of triethylamine to yield PM-567. The structure (Fig. 1) was confirmed by proton nuclear magnetic resonance spectroscopy. PM-567 is also commercially available and its absorption and fluorescent properties are well characterized.

Silanol-terminated PDMS (United Chemical Technologies) of low molecular weight (400–700) was used as the reactive polymer in the pyrromethene Polycerams. The hydroxyl end groups of PDMS can participate in the condensation reactions with hydrolyzed metal alkoxides or other silanol-terminated PDMS oligomers.

Typically, tetraethoxysilane (TEOS), PDMS, ethanol (EtOH), and H<sub>2</sub>O (acidified to 0.15M with HCl) were refluxed in a flask for 1 hour at a EtOH:H<sub>2</sub>O:TEOS molar ratio of 35:2:1. A base (triethylamine or pyridine) was added at base: acid mole ratio of 2:1 and the solution was mixed for 15 minutes. Then the PM-567 dye was added and the solution was concentrated.

Two types of samples were made from the solutions. Monoliths were made by pouring the solution in polypropylene beakers and drying at room temperature for 3 weeks. After polishing (described elsewhere) [10], the resulting Polyceram disks were 2 cm in diameter and 0.4 cm thick. All the monolith samples were made such that the solid contained 80 vol% PDMS

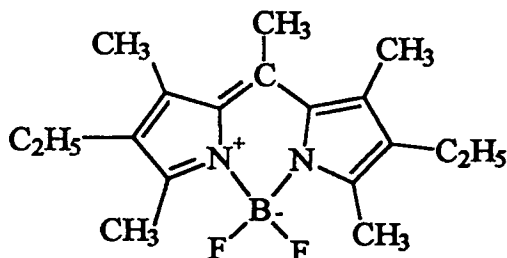


Figure 1. Structure of PM-567.

Table 1. Thick film PM-567 Polycerams with various polymer contents.

PDMS (vol%)	TEOS : PDMS mole ratio	Density* (gm/cm <sup>3</sup> )
99	0.2	—
90	2.1	1.11
80	4.7	1.23
60	12.6	1.32
40	25.8	1.38
20	75.7	1.40
0	∞	—

\*Measured by Archimedes' method.

and a dye concentration of  $6.8 \cdot 10^{-4} M$ . Thick films were also cast by drying a small amount of solution at 65 C. Samples were made at various PDMS contents in the solid Polyceram ranging from 0% to 99% by volume (see Table 1). A condensation catalyst such as dibutyltin dilaurate was often added. The thickness of these Polycerams was typically 0.5 mm.

Fluorescence photostability was measured by monitoring the fluorescence intensity as a function of the pump pulses from a Q-switched, frequency doubled Nd:YAG laser (Quanta-Ray DCR-11) at 532 nm with a pulse rate of 10 Hz, a pulse width of 6 ns, a pulse energy of 28 mJ, and a spot size of 0.6 cm in diameter. The samples were pumped while placed within a 6 inch integrating sphere. The exiting light was passed through color filters and a spectrometer in order to collect only the fluorescent light from sample. The spectrometer was adjusted to the wavelength which had the highest fluorescent intensity (near 577 nm). The intensity of the light exiting the spectrometer was monitored by a silicon detector. A schematic of the setup is shown in Fig. 2. UV degradation measurements were performed on the thick film Polycerams, and the details of the experimental method are described elsewhere [11].

## 3. Results and Discussion

### 3.1. Fluorescence Photostability

Figure 3 shows a fluorescence photostability curve obtained on a polished monolith. At a pump fluence of 0.10 J/cm<sup>2</sup>, the fluorescence intensity dropped in half after  $\approx 50,000$  pulses. Bleaching in the pumped area confirmed that dye degradation was occurring. Bleaching has also been observed by Rahn and King

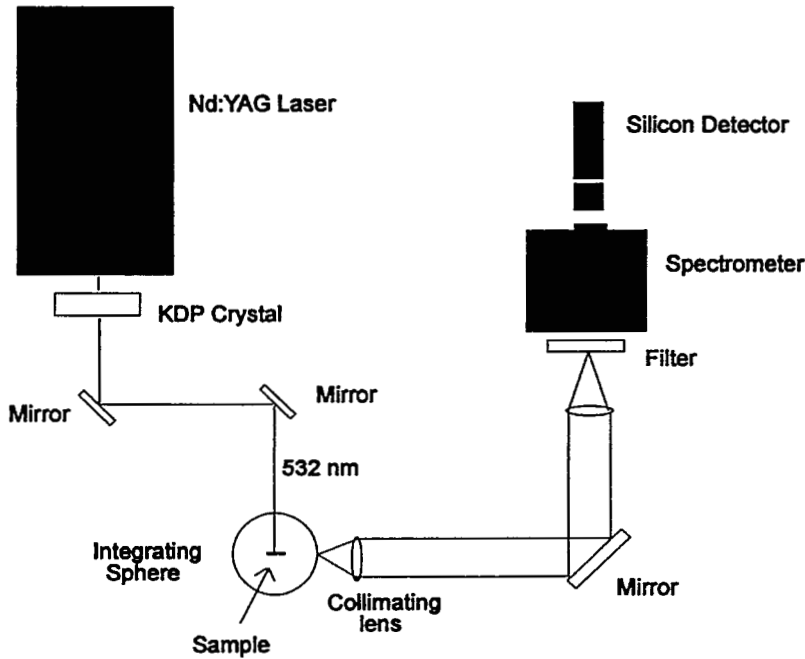


Figure 2. Schematic of the fluorescence photostability setup.

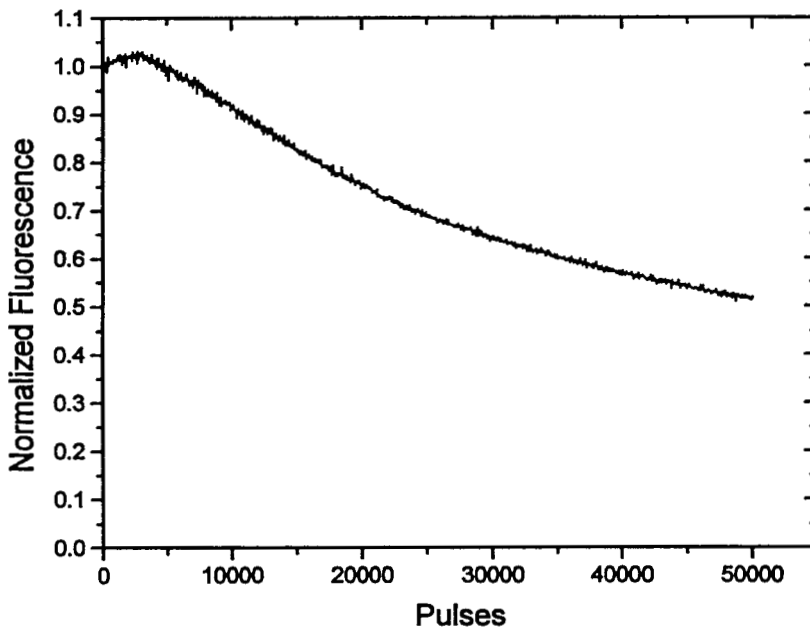


Figure 3. Normalized fluorescence as a function of pump pulses of a PM-567 Polyceram monolith.

in a silica:polymethylmethacrylate host [12]. The PM-567 Polycerams showed no signs of host damage, indicating that the dye, not the host, is limiting the photostability of the material. An unpolished sample,

pumped at much higher fluence of  $0.53 \text{ J/cm}^2$ , showed sample cracking and blackening near the surface, indicating host damage. The laser damage threshold for a polished sample is expected to be much higher.

Table 2. Photostability of PM-567 in various hosts and pump conditions.

Host/dye concentration ( <i>M</i> )	Pump characteristics		Sample thickness (mm)	Lifetime (50%) (pulse/s)	Ref.
	Pulse rate (Hz)	Fluence (J/cm <sup>2</sup> )			
Ormosil (TMOS:TMSPM:MMA)/ $2.0 \cdot 10^{-4}$	10	0.12	—	<12,000	[3]
	10	0.46	—	<1000	
Ormosil (VTEOS)/ $10^{-3}$	1	0.7 mJ/pulse	10	59,000	[6]
	5	0.7 mJ/pulse	10	14,000	
Ormosil (VTEOS)/ $5 \cdot 10^{-4}$	1	0.20	4	5000	[7, 13]
Polyceram (TEOS:PDMS)/ $6.8 \cdot 10^{-4}$	10	0.10	4	>50,000	Present work

TMSPM = 3-trimethoxysilyl propylmethacrylate, MMA = methyl methacrylate monomer, VTEOS = vinyltriethoxysilane.

Photostability of a sample depends not only on the laser dye and the host composition and structure, but also on factors such as the dye concentration, pump wavelength, pulse rate [6, 7], pump fluence [3], sample thickness [7], and geometry. With all these parameters, it is difficult to compare photostability measurements performed by different research groups. Photostability results on PM-567 in different solid hosts and varying pumping conditions are shown in Table 2. The present study has been concerned with fluorescence photostability, while the other results in the table represent laser lifetime. Both methods should provide valid measures of the photodegradation process.

### 3.2. Absorption Photostability by UV Degradation

With the addition of a condensation catalyst, it was possible to synthesize thick film Polycerams at various polymer contents. The 99 vol% PDMS sample was a very soft gel; and the hardness of the samples increased at lower polymer contents. Without a catalyst, only solutions with high inorganic content would gel. UV degradation of the PM-567 Polycerams at various polymer contents is illustrated in Fig. 4. The rate of dye degradation of the samples varied at short and long times. The short-term decay (<25 hours) was the fastest for the 0 and 99 vol% PDMS Polycerams. The

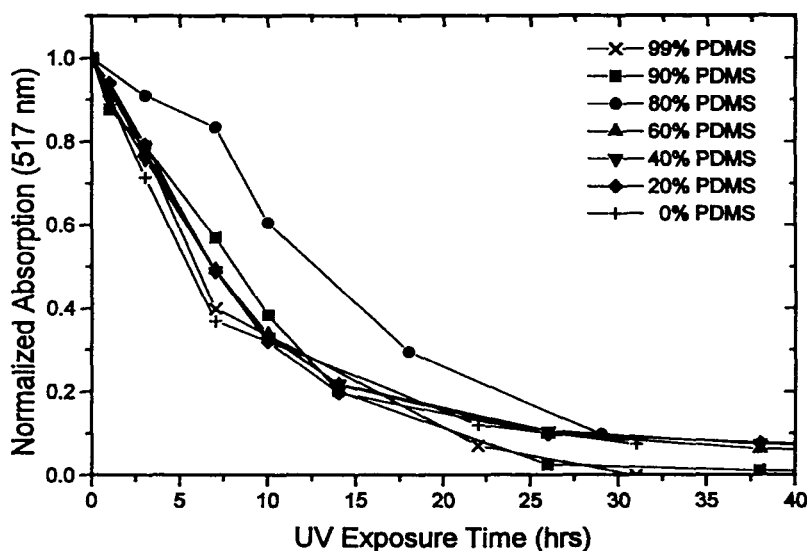


Figure 4. Normalized absorption at 517 nm upon UV lamp exposure for PM-567 Polycerams with different vol% PDMS.

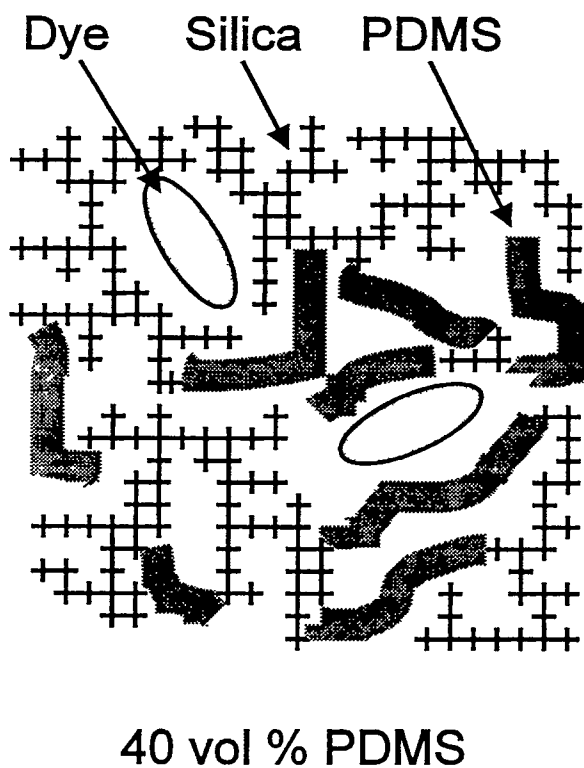
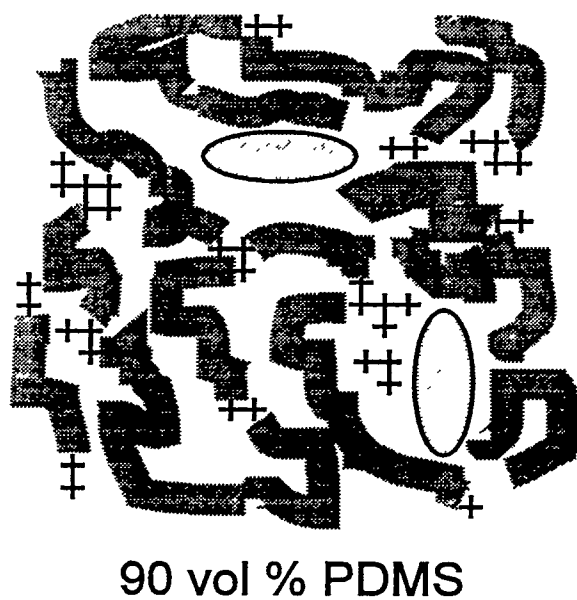


Figure 5. Proposed structures of PM-567 Polycerams with different vol% PDMS.

slowest rate of decay was observed at 80% PDMS; and the 20–60% PDMS samples were in between. At long times of UV exposure, the absorption of the dye in the high polymer Polycerams (90 and 99 vol%) dropped to less than 0.5%; while Polycerams with 0–80% PDMS exhibited a much slower rate of photodegradation and stabilized at about 7–8%. After UV exposure, samples with high inorganic contents were still orange colored and fluorescent, while samples with 90 and 99 vol% polymer were completely colorless.

A mechanism by which dye degradation takes place involves a chemical reaction between the photo-excited dye molecule and some impurity. Caging the dye and preventing dye diffusion or impurity diffusion to the dye has been proposed as a means of improving photostability. It is believed that the slow rate of decay over long times of UV exposure for samples with large inorganic contents is due to inorganic caging of the dye. At high polymer contents, the low degree of crosslinking results in very little or no caging, and hence all the dye molecules degrade; while at lower polymer contents, a portion of the dye molecules are caged. This is illustrated in the proposed structures of the PM-567 Polyceram at different polymer contents (Fig. 5).

At long times for the Polycerams with high inorganic contents, the percentage of dye molecules inorganically caged is low (7–8%) and does not increase with increasing inorganic content. The small amount of inorganic caging is attributed to the low solubility of dye PM-567 in the inorganic silica skeleton. Solubility parameters for PM-567 ( $\delta = 8.16 \text{ (cal/cm}^3)^{1/2}$ ), PDMS ( $\delta = 8.91 \text{ (cal/cm}^3)^{1/2}$ ), and the silica surface ( $\delta = 13.39 \text{ (cal/cm}^3)^{1/2}$ ) have been calculated by summing group contributions to the cohesive energies and molar volumes [14]. The silica surface was represented by a partially reacted TEOS, where Si is bonded to one ethoxide group and one hydroxyl group. The large disparity in the solubility parameters between the silica and the dye indicate that the dye is more likely to be found in the polymer phase, explaining the relatively low degree of inorganic caging. The low degree of dye caging in the samples with 0% PDMS (a xerogel) is attributed to dye agglomeration and dyes located within open pores of the silica network. Covalently bonding the dye into the silica network has been shown

to increase dye caging and reduce dye aggregation [10, 11].

The enhanced short term photostability at 80% PDMS is believed to be caused by greater organic-inorganic caging. Such caging can allow movement of species in and out the cage due to the high flexibility of PDMS chains. The activation energy for diffusion is expected to be higher than in a non-crosslinked environment and lower than in an inorganic cage.

## Acknowledgments

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